



Hydrodechlorination of *para* chloroacetophenone with water-repellent platinum catalysts in a water/ethanol mixed solvent



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ABSTRACT

To identify an effective catalyst for hydrodechlorination (HDC) reaction in an aqueous solvent, three types of modified Pt/SiO₂ catalysts were prepared using the water-repellent organosilane reagents of butyldimethylchlorosilane (BDMS), dimethyloctylchlorosilane (DMOS), and dimethyloctadecylchlorosilane (DMODS). The catalysts were characterized and their HDC activity toward *para*-chloroacetophenone (CLAP) was examined in an aqueous solvent.

The BET specific surface area, mesopore volume, platinum surface area, and high oxidation species of platinum surface of Pt/SiO₂-DMODS slightly decreased after the modification. Elemental analysis showed that 0.272 groups/nm² of the DMODS substituent were tethered on the catalyst surface.

Notably, in a water (35 mL)/ethanol (5 mL) mixed solvent under 1 MPa of hydrogen at 373 K for 60 min, the HDC reaction over the modified catalysts readily took place. From the difference in the extent of HDC product yields for the reactions, it was clear that the HDC activity of the catalysts decreased in the order Pt/SiO₂-DMODS \approx Pt/SiO₂-DMOS > Pt/SiO₂-BDMS \gg Pt/SiO₂. Furthermore, the turnover frequency (TOF) of Pt/SiO₂-DMODS (10.7 min⁻¹) was found to be more than fifty times that of Pt/SiO₂ (0.2 min⁻¹). These results indicate that the catalytic activity was significantly improved by the surface modification of the Pt/SiO₂ catalyst with the water-repellent organosilane reagents.

The high HDC activity of the modified catalysts is believed to result from the formation of a hydrophobic space on the catalytic support surface by the water-repellent organosilyl substituents. Therefore, more reactants in the aqueous solvent can interact with this space, leading to a significant increase in the number of collisions between the reactants on the active site.

The effects of the solvent composition and reaction temperature on the HDC activity of Pt/SiO₂-DMODS were also examined.

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1. Introduction

Recently, the Stockholm convention on persistent organic pollutants decided that countries attending the convention must be obliged to achieve the goal of environmentally sound management of polychlorinated biphenyl waste by 2028. Therefore, a method is urgently needed for decomposing such toxic chlorinated compounds. Among various degradation methods for chlorinated compounds, catalytic hydrogenolysis (hydrodechlorination, HDC) has the greatest potential as an environmentally benign technique because no harmful by-products such as dioxins are produced [1–3].

On the other hand, various organic solvents have been widely used in the chemical industry to elaborate chemical materials that support the comfortable lifestyle of mankind. However, the use of many organic solvents causes the release of hazardous materials such as volatile organic compounds and/or persistent organic waste that reduces the biodegradable activity in sewage plants. In addition, the release of organic solvents into the natural environment increases the biological oxygen demand and chemical oxygen demand values of river and sea water. Therefore, to preserve the global environment from the harmful consequences, a decline in the use of organic solvents and the use of alternative materials is an urgent global issue in the chemical industry. For example, if the disadvantages of water, in which organic compounds are generally insoluble, can be overcome, the use of water as a solvent and dispersion medium in the chemical industry would be favorable for conserving the environment. In fact, much attention has been focused on the development of alternative water-based organic transformations in recent years [4,5].

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For the reductive dechlorination of chloroaromatics in water, four main types of processes are possible:

1. The electrolytic method [6,7],
2. The subcritical method [8],
3. The water-gas-shift method [9,10], and
4. The common chemical method using a hydrogen and catalyst (that is, the HDC reaction) [11–45].

In these methods, a heterogeneous catalyst is typically used for the HDC reactions, where typical catalysts include: fly ash [11], Fe–Ni [12], Raney–Ni [13–17], Ni/C [18], Cu/C [18], Ru–Pd/TiO₂ [19], Ru/C [20], Rh/Al₂O₃ [1,21], Rh/C [1,21,22], Pd/zeolite-Y [23,30], Pd/Al₂O₃ [1,21,22,24–30], Pd/C [1,3,14–16,18,20–22,24,26,31–39], Rh–Pd/C [2], Pd/PS–PEG [4,5], Pd/TiO₂ [39], Pd/membrane polymer [40,41], Pd/Fe₃O₄ [43], Pt–Al/pillared clays [44], Pt/Al₂O₃ [21], and Pt/C [14,29,45].

In some studies of the HDC reaction of certain chloroaromatics, surface-modified catalysts were designed to increase the hydrophobicity on the catalytic surface or the mesopores of the support. Schüth et al. reported that Pd/zeolite-Y (hydrophobic support, pore size of 0.74 nm) was most resistant to deactivation by sulfite ion among Pd/zeolite-Y, Pd/ZSM-5, and Pd/MCM-41 for the HDC reaction of 1, 2-dichlorobenzene in groundwater containing sulfite ions, and showed that the effective issue was not the hydrophobicity, but the pore size of the support [23]. Likewise, A-Wedler et al. revealed that a Pd/Al₂O₃ catalyst coated with a silicone polymer (19% SE30 methylsilicone oil) showed the high reactivity in the HDC reaction of monochlorobenzene, as well as Pd/zeolite-Y [30].

However, because the main purpose of employing hydrophobicity on the catalytic surface was to protect the catalyst from sulfite ions existing in groundwater, both reactions were performed at a considerably low concentration (2–20 mg/L). In addition, in the latter example, because the silicon oil was only physically coated onto the catalyst surface and/or percolated through the pores of the support, it could possibly be released.

Furthermore, Nakao et al. reported that the HDC reaction of arylchlorides in 10% 2-propanol/water with ammonium formate at room temperature was effectively catalyzed by dispersed Pd-nanoparticles on the amphiphilic polystyrene-polyethylene glycol (PS-PEG) resin [4,5] because of the catalyst's ability to adapt to both the hydrophobic and hydrophilic properties of organic substrates.

Even though the investigation of the modification of catalyst supports has not been extensive, these studies show that it should be possible to improve HDC catalytic activity in aqueous media through the modification of the characteristics of the catalyst support.

In the present study, we prepared three types of surface-modified Pt/SiO₂ catalysts using water-repellent organosilane reagents, in which the organosilanes were associated with the silica surface on the catalytic support.

The HDC activities of these catalysts were examined in water/ethanol mixed solvents using *para*-chloroacetophenone (CLAP), which is resistant to chlorine atom removal in an organic solvent because of the preferential hydrogenation of the acetyl substituent over Pt/C [46] and Ru/C [47] catalysts, as a model chloroaromatic compound. In addition, because very interesting results were obtained for the HDC activity of these catalysts, the characteristics of a representative surface-modified catalyst were evaluated and compared with that of the unmodified Pt/SiO₂ catalyst.

2. Experimental

2.1. Materials

CLAP as a substrate was purchased from Tokyo Kasei Kogyo Co., Ltd. and purified by distillation before each run. HPLC grade distilled water and ethanol were obtained from Wako Jyunyaku Kogyo Co., Ltd. Silica gel (200–400 mesh, BET specific surface area: 296 m²/g; pore volume: 0.75 cm³/g) and hydrated platinum (II) tetraammine dichloride (Pt(NH₃)₄Cl₂·H₂O) were purchased from Sigma-Aldrich Co., Ltd. Butyldimethylchlorosilane (BDMS, C₄H₉Si(CH₃)₂Cl), dimethyloctylchlorosilane (DMOS, C₈H₁₇Si(CH₃)₂Cl), and dimethyloctadecylchlorosilane (DMODS, C₁₈H₃₇Si(CH₃)₂Cl) were obtained from Gelest, Inc. Except for the substrate, all solvents and catalyst materials were used without further purification.

2.2. Catalyst preparation

Silica gel (30 g) was soaked in an aqueous ammonia solution (0.1 mol/L, pH > 12) at room temperature for a week. The soaked silica was washed with deionized water (to pH 7) and methanol, and then dried at room temperature for one day. The Pt/SiO₂ catalyst was prepared via an ion-exchange reaction on the dried silica. Over the course of a week, the ammonium ions on the dried silica (15 g) were replaced with platinum (II) tetraammine ions ([Pt(NH₃)₄]²⁺, 1.1 g) of a 9 × 10^{−3} mol/L in a diluted ammonia solution. After filtration and drying as described above, an ion-exchanged catalyst precursor was obtained. The precursor (13 g) was calcined in dry air (flow rate of 100 mL/min) under 0.5 MPa at 523 K for 10 h. Following the calcination, the Pt/SiO₂ catalyst was subjected to hydrogenation under 0.5 MPa at 573 K for 14 h.

The surface of the Pt/SiO₂ catalyst was silylated using three types of organosilane reagents. After degassing at 423 K for 4 h, the bare Pt/SiO₂ catalyst (1.25 g) was soaked in an organosilane/toluene solution (2.5 g/50 mL) at 393 K for 27 h. Then, the catalyst in the solution was filtered and washed sequentially with toluene, water, and methanol until any excess organosilane and by-product hydrogen chloride were removed. Therefore, Pt/SiO₂-BDMS, Pt/SiO₂-DMOS, and Pt/SiO₂-DMODS catalysts were prepared from BDMS, DMOS, and DMODS, respectively.

2.3. Catalyst and product analysis

2.3.1. Catalysts

Physical measurements of the catalysts were performed. The metal content of the catalysts was determined using the inductively coupled plasma atomic emission spectroscopy (Shimadzu Co., CPS-8100) of dilute solutions, followed by the microwave irradiation of the catalysts in aqua regia and hydrofluoric acid at 503 K.

BET specific surface area and pore size distribution measurements were determined using the BELSORP-mini (BEL Japan, Inc.). After outgassing at 393 K for 8 h, a nitrogen adsorption isotherm was employed to determine the total surface area at 77 K [48]. The mesopore volume was measured using the Barrett–Joyner–Halenda (BJH) method [49].

The metal surface area, dispersion, and average metal particle size were obtained from gas chemisorption analysis of carbon monoxide (CO, BEL-METAL-3SP, BEL Japan Inc.). The samples (100 mg) were reduced in hydrogen at 473 K for 60 min. Following the reduction, the samples were heated by sweeping hydrogen with helium gas (flow rate of 50 mL/min) for 90 min, cooled to 323 K, and then subjected to CO chemisorption using a pulse (10% CO/He, ca. 0.13–0.14 mL at a time) titration procedure in a helium flow rate of 50 mL/min.

The elemental analysis of some of the catalysts was also performed using a conventional method (J-SCIENCE LAB Co., Ltd., JM10) to estimate the coverage of the organosilyl substituents on the surface.

Powder X-ray diffractograms were recorded with a D8-Focus (Bruker AXS K.K.) using nickel filtered Cu-K α radiation. The samples were mounted in a low background sample holder and scanned at a rate of 0.02°/step over $10 \leq 2\theta \leq 80^\circ$ at a scan rate of 0.06°/min at 298 K.

Temperature-programmed experiments were performed under oxidative (thermogravimetric-differential thermal analysis, TG-DTA) and reductive (temperature-programmed reduction by hydrogen, H₂-TPR) conditions. TG-DTA profiles were recorded with a TG-DTA 2020s (MAC Science Co., Ltd.); samples (25 mg) placed in a platinum crucible were heated in air at 10 K/min from room temperature to 1273 K. The H₂-TPR profile of the Pt/SiO₂-DMODS catalyst was recorded with an automatic temperature-programmed desorption spectrometer apparatus coupled to a mass spectrometer (TPD-1-ATw, BEL Japan Inc.). The sample (100 mg) was heated under a mixed gas of 5% H₂/He (60 mL/min) at 10 K/min up to 1073 K during the measurement.

X-ray photoelectron spectra were obtained from a ESCA 3400 spectrometer (Shimadzu Co.) in ex situ condition at a room temperature using non-monochromatic Mg-K α radiation (1253.6 eV) at a power of 200 W (20 mA, 10 kV) in a pressure of $< 10^{-6}$ Torr. The calibration of binding energies (BE) were referenced to the C1s peak at 285.0 eV [50].

2.3.2. Products

The products were analyzed using a gas chromatograph (Shimadzu Co., GC-14A) equipped with a wide bore capillary column (Varian, CP-Sil13CB, ID 0.53 mm \times length 100 m) and a FID. Helium gas was used as the carrier at a flow rate of 20 mL/min. An internal standard method with toluene was used to quantitatively analyze the reactions. Products were identified by gas chromatography–mass spectroscopy (Shimadzu Co., GC-MS5050QA) using a narrow bore capillary column (CP-Sil13CB, ID 0.25 mm \times length 60 m).

2.4. Reaction procedure

The catalyst (40 mg) in a test tube (Pyrex glass, 77 mL) was placed into a magnetically-stirred batch autoclave. The experimental reactor has been described previously [51]. After the reduction of the catalyst at a hydrogen flow rate of 100 mL/min under 0.5 MPa at 473 K, water (35 mL) was injected into the test tube on the autoclave at 373 K. A solution of CLAP (2×10^{-3} mol) in ethanol (5 mL) was then injected using 0.8 MPa hydrogen. The pressure was adjusted to 1.0 MPa, and the reaction was started. In the course of the reaction, the hydrogen pressure and temperature were controlled at 1.0 ± 0.05 MPa and 373 ± 1 K, respectively. The reaction products were periodically extracted through a pressure-resistant valve.

3. Results and discussion

3.1. Physical catalyst properties

3.1.1. N₂ adsorption

To obtain information on the surface transformation during catalyst modification, the physicochemical properties of both the bare catalyst (Pt/SiO₂) and catalyst modified with dimethyloctadecylchlorosilane (Pt/SiO₂-DMODS) were investigated. As can be seen in Table 1, the degree of metal loading varied slightly from 5.1% to 4.9% with modification by the organosilane, indicating that the metal was barely leached out after silylation. Otherwise, the specific

Table 1

Textural characteristic of Pt/SiO₂ and Pt/SiO₂-DMODS catalyst.

	Pt/SiO ₂	Pt/SiO ₂ -DMODS
N ₂ adsorption		
Metal loading [w/w %]	5.1	4.9
BET specific surface area [m ² /g]	243	228
Mesopore volume [cm ³ /g]	0.74 ^a , 0.76 ^b	0.70 ^a , 0.72 ^b
Pulse CO chemisorption		
Adsorption volume [cm ³ /g] ^c	2.0	1.2
Metal surface area [m ² /g]	4.3	2.6
Average metal particle size [nm]	3.3	5.2
Dispersion [%]	34	26
Elemental analysis [w/w %]		
Hydrogen	0.5	0.7
Carbon	0	2.4
Nitrogen	0	0
Oxygen	0.9	0.9
Ash	98.6	96.0

^a BJH method associated with absorption.

^b BJH method associated with desorption.

^c STP, 0.101 MPa and 273 K.

surface area and the mesopore volume decreased from 243 m²/g and 0.74 cm³/g to 228 m²/g and 0.70 cm³/g, respectively.

3.1.2. Pulse CO chemisorption

The features determined via pulse CO chemisorption were similar to those obtained via N₂ adsorption. As can be seen in Table 1, the adsorption volume of carbon monoxide on the Pt/SiO₂-DMODS catalyst (1.2 cm³/g) was slightly less than that on the Pt/SiO₂ catalyst (2.0 cm³/g), indicating a decrease in the metal surface area and metal dispersion degree, which is contrary to the enlargement of the metal particle size after modification. It is clear that the platinum particles on the support migrated and aggregated in spite of the heat treatment at a relatively low temperature of 393 K. It should be noted that the data for pulse CO chemisorption were calculated assuming a stoichiometric atomic ratio (CO/Pt = 1/1) and a spherical metal model on the silica support.

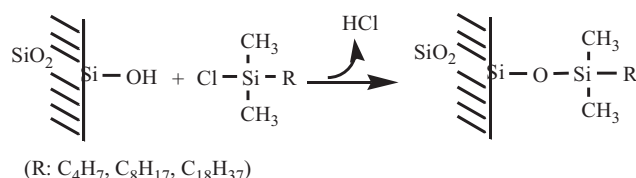
3.1.3. Elemental analysis

By comparing the results of the elemental analysis of the Pt/SiO₂ and the Pt/SiO₂-DMODS catalysts, the existence of an organic component on the catalytic support was revealed for the modified catalyst. In addition, the determination of a carbon content of 2.4 wt% (Table 1) confirmed the existence of a hydrocarbon component in the Pt/SiO₂-DMODS catalyst, while no organic substituents were observed in the Pt/SiO₂ catalyst. In the other modified catalysts and the Pt/SiO₂-DMODS catalyst, the covalent bond formation between the organosilanes and surface hydroxyl groups (silanol, -Si-OH) of silica was also expected. This process is described in Scheme 1.

3.2. Catalyst information

3.2.1. X-ray diffraction

To obtain further information on the catalyst surface and structure, X-ray diffraction analysis was performed for several different



Scheme 1. Covalent bond formation of alkylsilyl substituents on silica surface.

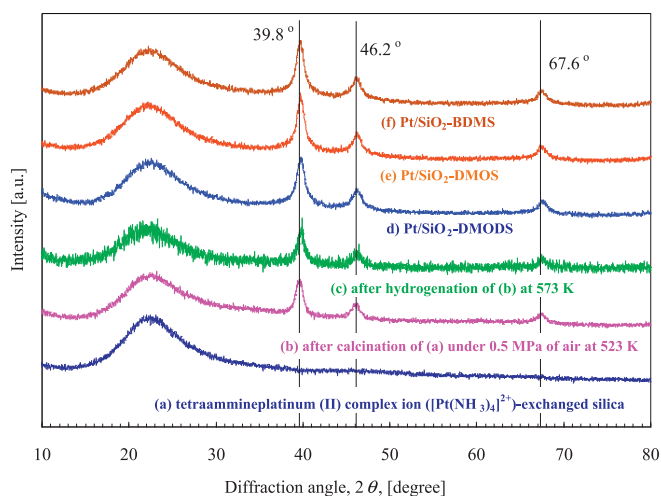


Fig. 1. X-ray diffraction pattern in the series of Pt/SiO₂ catalysts: (a) tetraammineplatinum (II) complex ion ([Pt(NH₃)₄]²⁺)-exchanged silica (b) after calcination of (a) under 0.5 MPa of air at 523 K (c) after hydrogenation of (b) at 573 K (d) Pt/SiO₂-DMODS (e) Pt/SiO₂-DMOS (f) Pt/SiO₂-BDMS.

Pt/SiO₂ catalysts (Fig. 1). Except for the ion-exchanged silica (first catalyst precursor, diffraction pattern (a)), platinum metal angles of 39.8°, 46.2°, and 67.6°, which were identified as the (1 1 1), (2 0 0), and (2 2 0) planes, respectively, were detected in the patterns for the series of catalysts (b), (c), (d), (e), and (f). Here the diffraction patterns (b) and (c) are for the catalyst after calcination and hydrogenation of (a) and (b), respectively. The catalysts with diffraction patterns (d), (e), and (f) were prepared by the surface modification of (c).

In spite of the oxidative heat treatment at 523 K, platinum oxide species such as PtO₂ were barely detected after calcination under 0.5 MPa of air (see diffraction pattern (b)).

3.2.2. Temperature-programmed analysis

For the representative catalysts, temperature-programmed profiles using thermogravimetric analysis (TGA) and differential thermal analysis (DTA) are shown in Fig. 2.

In the TG-DTA of Pt/SiO₂-DMODS, a 2.8 wt% weight loss and a large exothermic peak were observed at 500–750 K. This weight loss might be because of the oxidative decomposition of the dimethyloctadecylsilyl (DMODS) substituent tethered on the silica surface. In fact, the TGA plots agree well with those reported for titania and zirconia on which several organosilanes were grafted [53,54]. In the case of the Pt/SiO₂ catalyst, on the other hand, neither

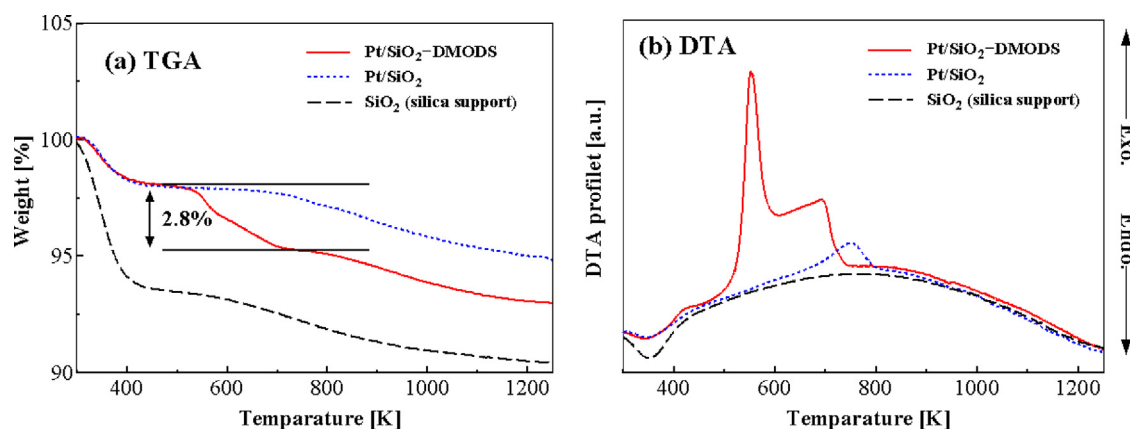


Fig. 2. Temperature-programmed oxidative profiles (TG-DTA) of catalysts: (a) weight loss (wt%) in the thermogravimetric analysis (TGA), (b) differential thermal analysis (DTA).

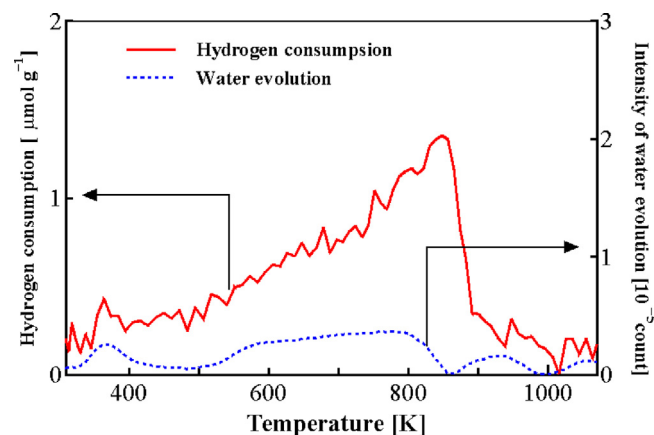


Fig. 3. Hydrogen consumption and water evolution in temperature-programmed reduction (H₂-TPR) of Pt/SiO₂-DMODS catalyst.

a weight loss nor an exothermic peak were observed at 500–750 K, although a small exothermic peak was detected at 750–800 K. In addition, no exothermic peak was observed for the silica gel support.

The surface coverage of an organosilane on HPLC column packing (octylsilyl or octadecylsilyl silica) is defined as Eq. (1). Therefore, this equation was used to estimate the surface coverage of the organosilane on the Pt/SiO₂-DMODS catalyst [53–57]:

$$\frac{C\%}{(100 \times n_c \times AW_c - C\% \times (MW_s - AW_H))} \times \frac{1}{S_{BET}} \quad (1)$$

where $C\%$ is the mass percentage of carbon atoms in the modified catalyst, n_c is the number of carbon atoms in the organosilane, AW_c is the atomic weight of carbon, MW_s is the molecular weight of the organosilane, AW_H is the atomic weight of hydrogen, and S_{BET} is the BET specific surface area. In this study, $C\%$ is 2.4 wt%, n_c is 20, AW_c is 12.01, MW_s is 311.64, AW_H is 1.008, and S_{BET} is 228 m²/g. Using Eq. (1), therefore, the surface coverage with the DMODS substituent was calculated to be 0.452 μmol/m², which means that 0.272 groups of the organosilyl substituent are covalently connected to an oxygen atom on the silica support per 1 nm² of surface area.

To evaluate the thermal stability of Pt/SiO₂-DMODS as a function of the upper limit of the heat-treatment temperature during the pre-activation of the catalysts, the catalyst was also subjected to H₂-TPR.

The hydrogen consumption profile is shown in Fig. 3 along with the water evolution profile. The amount of water evolution is

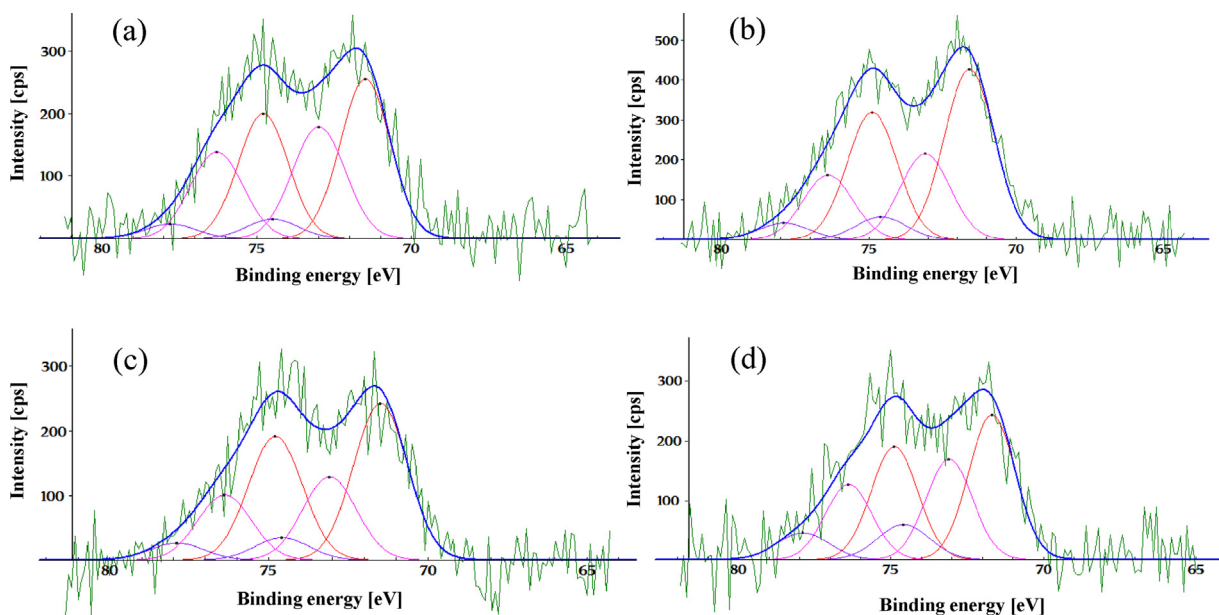


Fig. 4. Binding energies in X-ray photoelectron analyses for the series of Pt/SiO₂ catalysts: (a) Pt/SiO₂ (b) Pt/SiO₂-DMODS (c) Pt/SiO₂-DMOS (d) Pt/SiO₂-BDMS.

simply expressed as the ionic intensity (counts $\times 1/10^5$) as the reliability of the intensity of the quantitative analysis is low because of the strong adsorptive properties of water vapor on the inside wall of the metal plumbing in the apparatus.

While a small amount of hydrogen consumption was observed at 360 K because of the desorption of physisorbed water, on the whole, hydrogen gas consumption increased gradually until 860 K, and then rapidly decreased up to 900 K. Water evolution corresponded to the profile of the hydrogen consumption up to 860 K, and consisted of four sections at 300–473 K, 500–860 K, 860–1000 K, and above 1000 K. Therefore, it was confirmed that the catalyst pre-activation at 473 K is most suitable for avoiding the degradation of the organosilyl substituents on the catalytic surface.

3.2.3. X-ray photoelectron analysis

To investigate an oxidation state on a platinum surface dispersed on silica support, X-ray photoelectron analysis (XPS) was performed for both the Pt/SiO₂ catalyst and all the modified Pt/SiO₂ catalysts, as shown in Fig. 4. All the deconvolution peaks were fitted by symmetry Gaussian functions after a remove of Shirley background. The BE peaks of 71.6 eV and 74.9 eV were assigned to 4f_{7/2} and 4f_{5/2} of metallic platinum (Pt⁰), respectively, as M.Y. Kim et al. suggested for the 4.3%-Pt/SiO₂ catalyst [50]. In addition, two different convoluted BE peaks were also observed at first pair (4f_{7/2} and 4f_{5/2}) of 73.1 eV and 76.4 eV, and next ones of 74.6 eV and 77.9 eV, which were assigned to bivalent species (PtO: Pt²⁺), and tetravalent species (PtO₂: Pt⁴⁺), respectively [52].

Moreover, components of oxidation states of the platinum surface were checked. From the area of these deconvoluted peaks, components for the Pt/SiO₂ were calculated to 53% (Pt⁰), 40% (Pt²⁺), and 7% (Pt⁴⁺), respectively. On the other hand, those for the Pt/SiO₂-DMODS varied to 61% (Pt⁰), 31% (Pt²⁺), and 8% (Pt⁴⁺), respectively. A similar tendency was also observed for Pt/SiO₂-DMOS, which was calculated to 60% (Pt⁰), 31% (Pt²⁺), and 8% (Pt⁴⁺), respectively. These results indicate bivalent species of platinum oxides as PtO on platinum surface decreased after the modification using organic silanes. In contrast, components for the Pt/SiO₂-BDMS varied to 52% (Pt⁰), 35% (Pt²⁺), and 13% (Pt⁴⁺), respectively. This phenomenon apparently disagree with those for the Pt/SiO₂-DMODS and the Pt/SiO₂-DMOS, meaning that tetravalent species as PtO₂ increased after modification.

3.3. Hydrodechlorination

To examine the HDC activity of the modified and unmodified catalysts, CLAP was used as a substrate and reacted in an aqueous solvent.

3.3.1. HDC reaction over Pt/SiO₂

In our previous study [46], we reported that the HDC rate of CLAP in a hydrocarbon solvent over a Pt/C catalyst was considerably slow because of the high electron-withdrawing properties of the acetyl substituent at the *para*-position. It was expected that the HDC reactivity in an aqueous solvent would be even lower than that in a hydrocarbon solvent because CLAP is barely soluble in a water/ethanol mixed solvent.

As shown in Table 2, when the Pt/SiO₂ catalyst was used for the reaction of CLAP in a water (35 mL)/ethanol (5 mL) mixed solvent, only 12% of the reactant was converted to 4-chloro- α -methylbenzylalcohol (CMBA), and the HDC of CLAP barely proceeded, although a trace amount of acetophenone (AP) was detected. The variation of reactant and products yields with reaction time for the HDC reaction is also described in Fig. 5.

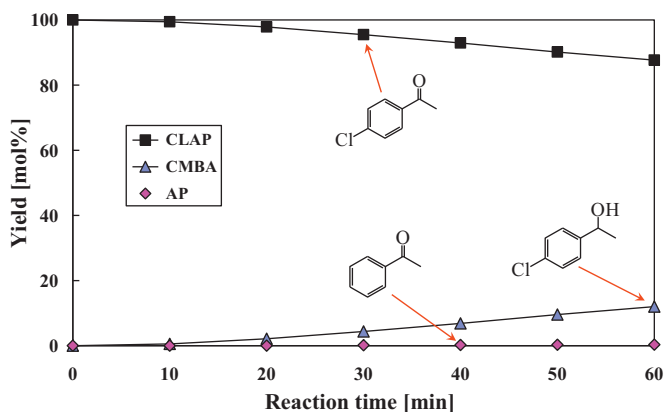
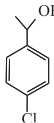
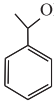
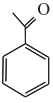
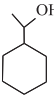
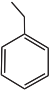
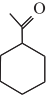
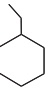
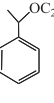


Fig. 5. Hydrodechlorination reaction of *para*-chloroacetophenone over Pt/SiO₂ catalyst in water-ethanol solution (water/ethanol = 35 mL/5 mL) under H₂ 1.0 MPa at 373 K.

Table 2
HDC reaction of *para*-chloroacetophenone over modified Pt/SiO₂ catalysts.

Catalyst	Conversion [mol%] ^a	Yield of HDC products [mol%] ^a	Products distribution [mol%] ^a							
			CMBA ^b	MBA ^b	AP ^b	CHEL ^b	EB ^b	ACH ^b	ECH ^b	EMBE ^b
										
Pt/SiO ₂	12	≈ 0	12	n.d. ^c	trace	n.d. ^c	n.d. ^c	n.d. ^c	n.d. ^c	n.d. ^c
Pt/SiO ₂ -BDMS	89	67	22	44	5	2	13	2	trace	2
Pt/SiO ₂ -DMOS	83	72	11	43	5	5	13	4	trace	2
Pt/SiO ₂ -DMODS	88	72	15	47	3	7	9	4	trace	2

^a CLAP: *para*-chloroacetophenone (2×10^{-3} mol), catalyst (0.04 g), in the mixed solvent of water (35 mL)/ethanol (5 mL) under H₂ 1 MPa at 373 K for 60 min.

^b CMBA: 4-chloro- α -methylbenzylalcohol, MBA: α -methylbenzylalcohol, AP: acetophenone, CHEL: 1-cyclohexylethanol, EB: ethylbenzene, ACH: acetylcyclohexane, ECH: ethylcyclohexane, EMBE: ethyl- α -methylbenzylether, respectively.

^c Not detected.

The low HDC activity of the Pt/SiO₂ catalyst is likely due to the fact that water interacts with the hydroxyl groups on the silica support, forming hydrogen bonds, thereby preventing the CLAP from reaching the platinum metal surface.

3.3.2. HDC reaction over modified Pt/SiO₂

To improve the low HDC activity of the Pt/SiO₂ in an aqueous solvent, new modified catalysts were prepared with water-repellent reagents immobilized on the silica support of the Pt/SiO₂ system. That is, three types of catalysts were prepared using organosilane reagents of BDMS (C4: carbon number of the main carbon chain), DMOS (C8), and DMODS (C18) are abbreviated as Pt/SiO₂-BDMS, Pt/SiO₂-DMOS, and Pt/SiO₂-DMODS catalysts, respectively. The results for the HDC reactions of CLAP over these modified catalysts are summarized in Table 2. In addition, as a representative result, the product variation with reaction time for the HDC reaction of CLAP over the Pt/SiO₂-DMODS catalyst is shown in Fig. 6.

Using the Pt/SiO₂-DMODS catalyst, an 88% conversion of CLAP was achieved in 60 min, and the sum of the yields of the different HDC reaction products was 72%, with the following product distribution: α -methylbenzylalcohol (MBA) 47%, CMBA 15%, ethylbenzene (EB) 9%, 1-cyclohexylethanol (CHEL) 7%, acetylcyclohexane (ACH) 4%, AP 3%, ethyl- α -methylbenzylether (EMBE) 2%, and ethylcyclohexane (ECH) < 1%. With the Pt/SiO₂-BDMS and Pt/SiO₂-DMOS catalysts, the product distributions were similar to that obtained with the Pt/SiO₂-DMODS catalyst. Overall, the HDC activity of these catalysts decreased in the following order: Pt/SiO₂-DMODS \approx Pt/SiO₂-DMOS > Pt/SiO₂-BDMS \gg Pt/SiO₂.

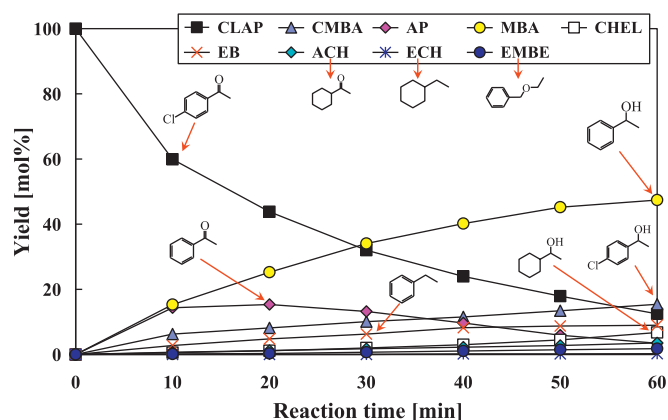


Fig. 6. Hydrodechlorination reaction of *para*-chloroacetophenone over Pt/SiO₂-DMODS catalyst in water-ethanol solution (water/ethanol = 35 mL/5 mL) under H₂ 1.0 MPa at 373 K.

To compare the difference in the quantitative activity of Pt/SiO₂ and Pt/SiO₂-DMODS, the turnover frequency (TOF) was calculated. On the basis of the overall conversion at 60 min, the TOF of the Pt/SiO₂-DMODS (12.9 min^{-1}) was fairly superior to that of the Pt/SiO₂ (2.2 min^{-1}), where the TOF is defined as “the atom ratio of substrate/active metal” per unit time, and the amount of the active metal atom is that of the surface atom determined from the pulse CO chemisorption. Furthermore, when the TOF was restricted to the gross yield of HDC products, the TOF of Pt/SiO₂-DMODS (10.7 min^{-1}) was more than fifty times that of Pt/SiO₂ (0.2 min^{-1}). These results suggested that the catalyst activity for HDC reaction improved predominantly because of the bonding of the hydrophobic organosilyl substituents to the support surface. Such an image of a hydrophobic space on catalyst surface was illustrated in Fig. 7.

The reactivity of CLAP over the modified catalysts was influenced by the following two factors. (1) Steric hindrance: Although CLAP should rightfully interact with a platinum metal at the position of the acetyl group possessing abundant electrons, the accession of the bulky acetyl group of CLAP onto the modified catalytic surface was prevented by the existence of closely-spaced alkylsilyl groups on the modified catalytic surface. (2) Hydrogen bonding: Because of the formation of hydrogen bond between the hydrogen atom of the water molecule and oxygen atom of the carbonyl group in the acetyl group of CLAP, the acetyl group of CLAP in the aqueous solvent may be oriented on the upper side of the benzene ring against the catalytic surface (active platinum surface), thereby leading to the interaction of CLAP with the active site of platinum in the vicinity of the chlorine atom, rather than with the acetyl group.

Furthermore, the above perspective for the reactivity of CLAP might be supported from XPS spectra of both the bared Pt/SiO₂ and the Pt/SiO₂-DMODS catalysts (Fig. 4). That is, when the latter modified catalyst is compared with the former bared catalyst, both the increase of the Pt⁰ state (8%) and the decrease of the Pt²⁺ state (9%) after the silylation of the Pt/SiO₂ catalyst using DMODS means the increase of metallic platinum being the main catalytic component on the Pt/SiO₂-DMODS catalyst. In other words, it might be suggested that the oxidation states of platinum metal plays a role for assisting the HDC reaction of CLAP smoothly. An expected reaction mechanism was illustrated in Fig. 8.

3.3.3. Effect of the carbon chain length of the modified catalysts on HDC activity

As can be seen in Table 2, HDC reaction was promoted with the Pt/SiO₂-BDMS (C4) and Pt/SiO₂-DMOS (C8) catalysts as well as the Pt/SiO₂-DMODS (C18) catalyst. However, the sum of the yields of the HDC products (67%) of the Pt/SiO₂-BDMS (C4) catalyst was

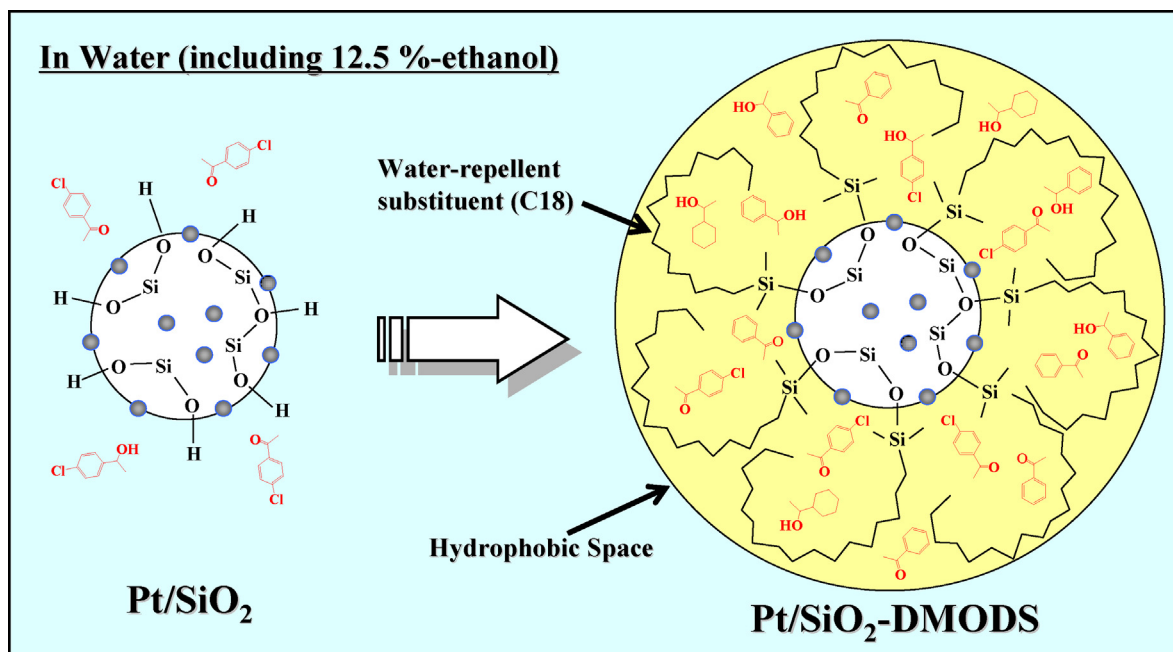


Fig. 7. Schematic illustration for extended hydrophobic space on modified catalyst surface.

somewhat lower than that (72%) over the Pt/SiO₂-DMODS (C18) catalyst. On the other hand, the yield of CMBA over the Pt/SiO₂-BDMS (C4) and Pt/SiO₂-DMODS (C18) catalysts were 22% and 15%, respectively, and the yield over the former catalyst was one and half times that over the latter catalyst. These differences in the product yields might indicate that more than eight carbon atoms are necessary for sufficiently promoting the HDC reaction of the CMBA intermediate. Notably, no significant difference was observed for the yields of HDC products using the Pt/SiO₂-DMOS and Pt/SiO₂-DMODS catalysts.

In water as a solvent, it is likely that the long alkyl chain binding with the support surface has a tendency to bend its tip down to the silica surface to reduce the interfacial tension with the water. Therefore, an effective hydrophobic space for the HDC reaction might be formed on the catalyst surface. Because the HDC product yield of Pt/SiO₂-DMOS (72%) is the same as that for Pt/SiO₂-DMODS (Table 2), it is expected that there is no difference in the substantive magnitude of the hydrophobic space between C8 and C18 alkyl chain lengths. In fact, Uozumi discovered that the hydrophobic space that was created by the bending of long organic chains of polyethylene glycol (PEG) on polystyrene (PS) resin behaved very effectively as a hydrophobic reaction field in water [58]. Therefore, his group was successful in performing several types of organic reactions catalyzed by Pd-complexes immobilized at the tip of an organic chain on the PEG-PS resin. These results suggest that, in the present reaction, the retention ability of the catalyst surface for CLAP is very important for increasing the HDC rate in water, and that a large volume of hydrophobic space is required on the catalyst surface.

From results of XPS (Fig. 4), components of platinum oxidation states for Pt/SiO₂-DMOS (C8) are similar to those of Pt/SiO₂-DMODS (C18). On the other hand, the decrease of Pt⁰ state (-9%) was observed in components for the Pt/SiO₂-BDMS (C4) after the silylation when comparing with Pt/SiO₂-DMODS (C18). At the present, the reason for the difference of oxidation states on the platinum surface of Pt/SiO₂-BDMS (C4) with those of both Pt/SiO₂-DMOS (C8) and Pt/SiO₂-DMOS (C18) is not clear, and the more detailed investigation is required. However, the increase of high-valent platinum states on the Pt/SiO₂-BDMS that is decreased in the metallic part on

the catalytic component agrees well with the decrease of HDC products yields and the increase of CMBA yield over the Pt/SiO₂-BDMS (C4) as mentioned above. This tendency indicates that the oxidation state of platinum is one of the factors for the HDC reaction of CLAP as well as organic chain length of substituent.

3.3.4. Effect of reaction temperature on HDC reactivity

The effect of the reaction temperature on the HDC reactivity over the Pt/SiO₂-DMODS catalyst was examined in the mixed water (35 mL)/ethanol (5 mL) solvent, and the results are presented in Table 3.

Although the highest total conversion (91%) was obtained in the reaction of CLAP over the Pt/SiO₂-DMODS catalyst at a reaction temperature of 363 K, overall, a high conversion value above 80% was observed in the reaction temperature range from 363 to 393 K. On the other hand, the product yield of the HDC reaction reached 69–73% in this temperature range. However, from the standpoint of the purpose of the present study, the HDC reaction at 373 K might be most appropriate for improving the catalytic activity because the HDC product yield at 373 K (72%) is better than that at 363 K (69%). At reaction temperatures above 403 K, both the conversion and HDC product yield decreased gradually from 68% to 23% and 58% to 23%, respectively.

The decrease in the catalytic activity at reaction temperatures above 403 K may be attributed to the degradation of the hydrophobic reactive space because the hydrolysis of the O–Si bond between the silica support and the alkylsilyl substituent is promoted at higher temperatures, which would lead to an increase in the rate of elimination of the substituent from the catalyst surface.

3.3.5. Effect of the ethanol ratio in the mixed solvent on HDC reactivity

The effect of the ethanol ratio in the water/ethanol mixed solvent on the HDC reactivity of the catalysts was examined for water/ethanol ratios ranging from 39/1 to 30/10.

As shown in Table 4, both the total conversion and the HDC product yield increased with the ethanol ratio in the concentration range described above. In particular, with a relatively higher ethanol content in the mixed solvent, CLAP was easily converted

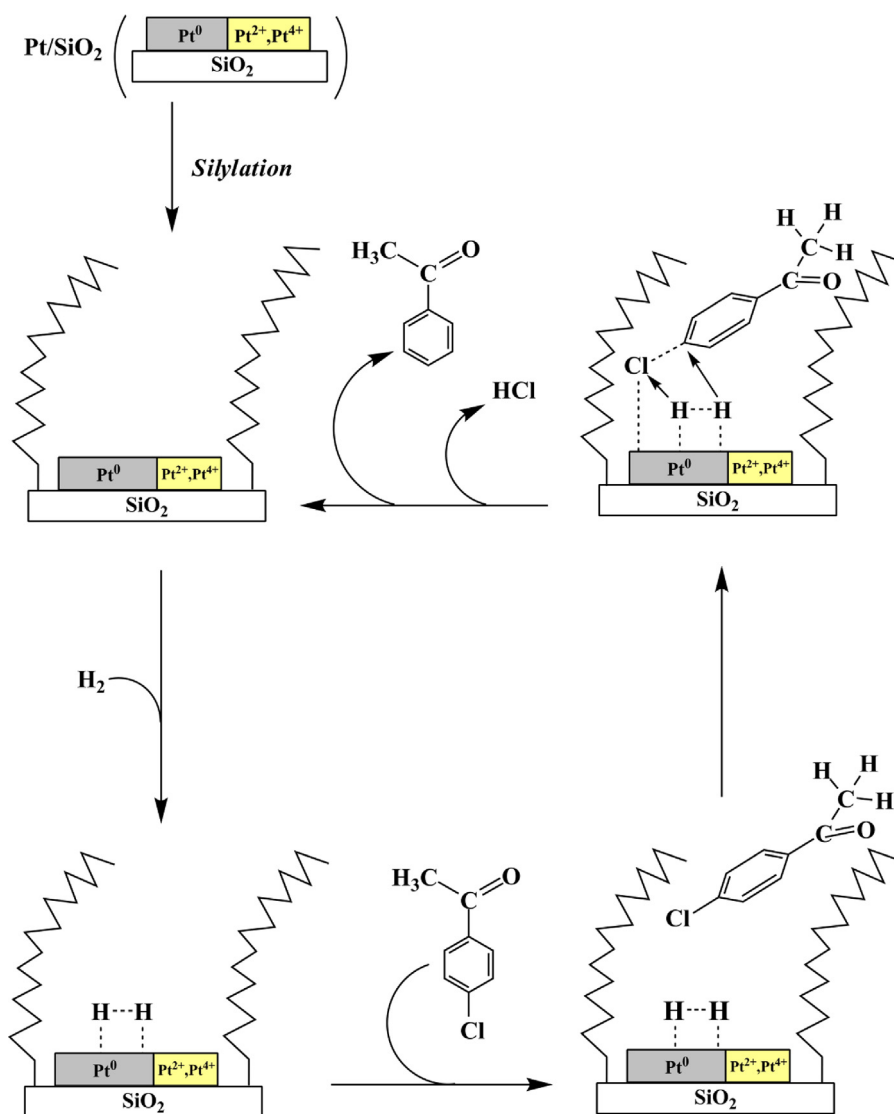


Fig. 8. An expected reaction mechanism on platinum surface.

Table 3

Effect of the reaction temperatures on the HDC reaction of *para*-chloroacetophenone over Pt/SiO₂-DMODS catalyst.

Temperature [K]	Conversion [mol%] ^a	Yield of HDC products [mol%] ^a	Products distribution [mol%] ^a							
			CMBA ^b 	MBA ^b 	AP ^b 	CHEL ^b 	EB ^b 	ACH ^b 	ECH ^b 	EMBE ^b
353	61	29	31	20	4	1	3	1	n.d. ^c	trace
363	91	69	22	53	2	4	6	3	trace	1
373	88	72	15	47	3	7	9	4	trace	2
383	84	73	11	30	4	7	22	6	trace	3
393	80	72	8	16	4	9	30	9	1	3
403	68 ^d	58	10	17	6	4	19	7	trace	4
423	44 ^d	33	10	9	15	1	3	2	n.d. ^c	2
473	23	23	trace	n.d. ^c	22	n.d. ^c	trace	n.d. ^c	n.d. ^c	n.d. ^c

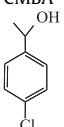
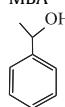
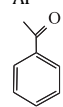
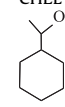
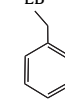
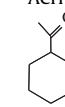
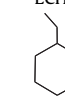
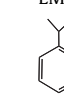
^a CLAP: *para*-chloroacetophenone (2×10^{-3} mol), Pt/SiO₂-DMODS catalyst (0.04 g), in the mixed solvent of water (35 mL)/ethanol (5 mL) under H₂ 1 MPa for 60 min.

^b CMBA: 4-chloro- α -methylbenzylalcohol, MBA: α -methylbenzylalcohol, AP: acetophenone, CHEL: 1-cyclohexylethanol, EB: ethylbenzene, ACH: acetylcyclohexane, ECH: ethylcyclohexane, EMBE: ethyl- α -methylbenzylether, respectively.

^c Not detected.

^d Unknown product was observed by 1–2%.

Table 4Effect of the solvent ratios of water/ethanol on the HDC reaction of *para*-chloroacetophenone over Pt/SiO₂-DMODS catalyst.

Water/ethanol [mL/mL]	Conversion [mol%] ^a	Yield of HDC products [mol%] ^a	Products distribution [mol%] ^a							
			CMBA ^b 	MBA ^b 	AP ^b 	CHEL ^b 	EB ^b 	ACH ^b 	ECH ^b 	EMBE ^b 
30/10	93	86	7	41	2	3	31	3	2	3
33/7	88	75	13	44	1	4	18	4	1	3
34/6	90	76	14	49	3	5	13	4	trace	2
35/5	88	72	15	47	3	7	9	4	trace	2
36/4	82	61	21	40	4	5	9	3	n.d. ^c	1
37/3	73	40	34	26	4	2	6	2	n.d. ^c	trace
39/1	67	36	31	26	4	1	4	1	n.d. ^c	trace

^a CLAP: *para*-chloroacetophenone (2×10^{-3} mol), Pt/SiO₂-DMODS catalyst (0.04 g), under hydrogen pressure 1 MPa at 373 K for 60 min.^b CMBA: 4-chloro- α -methylbenzylalcohol, MBA: α -methylbenzylalcohol, AP: acetophenone, CHEL: 1-cyclohexylethanol, EB: ethylbenzene, ACH: acetylcyclohexane, ECH: ethylcyclohexane, EMBE: ethyl- α -methylbenzylether, respectively.^c Not detected.

to dechlorinated compounds such as MBA, EB, and ACH, indicating that the hydrogenolysis of the C–Cl bond in CLAP proceeded smoothly.

When the ethanol ratio in the mixed solvent is increased, in general it is expected that the lipophilic properties of the mixed solvent increase while the viscosity of the solvent decreases. As a result, both the solubility of the substrate and the mass transfer in the mixed solvent are improved.

Therefore, in the present case, it is suggested that CLAP is moved to the vicinity of the catalytic surface where the hydrophobic space is formed by the alkylsilyl substituents, and then the number of collisions of the reactant with the active site is increased. In other words, it is likely that the hydrophobic space on the catalytic surface swelled and/or expanded in the presence of the ethanol, creating a larger hydrophobic space in the aqueous solvent where a greater number of solvated substrates, including both reactants and intermediates, could accumulate.

However, use of excess ethanol also promoted undesirable reactions. That is, ethanol reacted with the HDC product MBA to form EMBE, indicating that an optimal amount of ethanol must be used in the reaction.

4. Conclusions

1. To find an effective catalyst for the HDC reaction in an aqueous solvent, three types of modified catalysts were prepared via the silylation of a Pt/SiO₂ catalyst with BDMS, DMOS, and DMODS. The HDC activity of these modified catalysts was examined from the standpoint of the HDC reaction of CLAP in a water/ethanol mixed solvent.
2. The BET specific surface area, mesopore volume, and platinum surface area of the Pt/SiO₂-DMODS catalyst were slightly decreased after the modification. On the basis of the elemental analysis, it was determined that 0.272 groups/nm² of the dimethyloctadecylsilyl substituent were tethered to the catalyst surface. The metal particles on the silica support were slightly sintered after silylation with the organosilane reagent. The H₂-TPR profile indicated that a catalyst pre-activation temperature of 473 K was most suitable so that degradation of the organosilyl reagents could be avoided.
3. In the water (35 mL)/ethanol (5 mL) mixed solvent under 1 MPa of H₂ at 373 K for 60 min, the HDC reaction of CLAP over these modified catalysts occurred smoothly, and dechlorinated products were obtained in good yield (67–72%). On the other hand, when the unmodified Pt/SiO₂ was used as a catalyst, HDC

products were barely observed under the same reaction conditions. In these reactions, the HDC activity of the catalysts decreased in the following order: Pt/SiO₂-DMODS \approx Pt/SiO₂-DMOS $>$ Pt/SiO₂-BDMS \gg Pt/SiO₂. These results suggest that more than eight carbon atoms are necessary for achieving effective HDC reaction of organic chlorinated substrates in an aqueous solvent.

4. For all the catalysts, three types of platinum oxidation states were observed as metallic state, bivalent state, and tetravalent state. After the silylation of a Pt/SiO₂ catalyst, the increase of metallic platinum (7–8%) and the decrease of bivalent state (8–9%) were observed for Pt/SiO₂-DMODS, Pt/SiO₂-DMOS, thereby contributing to the HDC reaction of CLAP smoothly.
5. The TOF value of Pt/SiO₂-DMODS (10.7 min^{-1}) is more than fifty times that of Pt/SiO₂ (0.2 min^{-1}). This result demonstrates that the significantly enhanced HDC activity in the water/ethanol mixed solvent was brought about by modification of the Pt/SiO₂ catalyst.
6. Under the same reaction conditions described above, the HDC activity of the Pt/SiO₂-DMODS catalyst was maximized from 363 to 393 K, and increased with the ethanol volume ratio in the mixed solvent, although more than 10% ethanol in the mixed solvent was required to significantly promote the HDC reaction.
7. The large improvement in the HDC activity of the modified catalysts is believed to result from the creation of an effective hydrophobic space for the HDC reaction on the catalyst surface by the water-repellent organosilanes. Therefore, the ability of the catalyst surface to retain CLAP is increased considerably, and the surface concentration of the reactant and the number of collisions of the reactant with the active site is also increased significantly in the aqueous solvent.

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